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(54) **Low toxicity oil base mud systems**

(57) A low toxicity oil base mud which comprises (a) a petroleum oil containing less than 20 wt% aromatic hydrocarbons and neutralized sulphonated EPDM terpolymer for imparting viscosity to the oil and (b) a minor amount of water emulsified as an internal phase in the oil.

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LOW TOXICITY OIL BASE MUD SYSTEMS

The present invention relates to low toxicity oil based mud systems used in the oil industry and in particular to a viscosified oil based mud system.

In the exploration for and production of petroleum resources, a variety of base oils are used for the formulation of drilling fluids, spotting fluids, packer fluids, casing packs, and workover and completion fluids referred to herein collectively as drilling fluid or drilling mud. Because of its low cost and relative ease of viscosification, diesel oil has been the main hydrocarbon component in the oil base muds. However, the aromatic components of diesel oil are known to be toxic to certain marine animal and plant life. Accordingly, in recent years, there has been activity to develop low-toxicity oils for use in oil base muds. This activity has identified a number of oils low in aromatic content and mineral oils useful in drilling muds.

The need for a low-toxicity drilling mud is reflected by legislation governing oil base mud systems. In order to counteract the adverse environmental effects resulting from certain oil base drilling fluids, the U.S. and other governments have enacted laws and regulations, typified by the following:

- 1) Pollution is defined by 1976 EPA Regulations (Title 40, Chapter One, Part 110) as sheen, film or discoloration of surface water or adjoining shore line.

- 2) Section 311 of the Amended Federal Water Pollution Control Act of 1977 prohibits any oil discharge causing such pollution.

- 3) Section 402 of the Water Pollution Control Act regulates the discharge of drill cutting via national pollution discharge elimination system permits. These permits allow for the release of drill cuttings provided that any oil release from the cuttings does not cause a sheen or discoloration of the surface

water.

4) In the North Sea, interim regulations by the UK Department of Agriculture and Fishery allows for the discharge of diesel oil based drilling cuttings containing less than 5 weight percent diesel. Where a mineral oil is used as the base oil, cuttings may contain up to 15 percent oil by weight.

5) The release of toxic substances into contiguous or navigable waters is also prohibited by Section 311 of the Amended Federal Water Pollution Control Act of 1977.

In summary, it can be seen that by the above regulation, contamination by oil mud is regarded as a serious matter. As mentioned above, industry has responded to these regulations by producing low toxicity oil muds.

It has been found however that many of the typical oil base mud additives display reduced effectiveness in muds formulated from the low-toxicity oils. A particular problem with low-toxicity oils is the difficulty with which they can be viscosified. Viscosifiers for oil base muds are described in a paper presented at the 1984 meeting of the International Association of Drilling Contractors, March 29-31, entitled "An Overview of Low-Toxicity Oils" by Jack Cowan and Tom Brookey. They include the emulsified water fundamentally present in the mud and added soaps, asphalts, finely divided inert solids, and most commonly organophilic clay derivatives. A number of patents also disclose the use of viscosifiers in oil base muds. See for example U.S. Patents 4,425,455; 4,447,338; 4,425,462; and 4,442,011. These additives have not proven reliable in the viscosification of oil base muds compounded from low toxicity base oils and there is a need for improved materials for this use.

It has been discovered that certain lightly sulfonated elastomers are effective viscosifiers for low aromatic oils and are non-toxic. Accordingly, the present invention provides an oil base drilling fluid which comprises

- (a) a petroleum oil with a low aromatic hydrocarbon content
- (b) a minor amount (e.g. 1-40 vol %) of water dispersed

or emulsified as an internal phase in said oil; and

(c) an effective amount of a neutralized sulfonated elastomeric polymer for viscosifying the hydrocarbon liquid.

For purposes of ecology, the preferred petroleum oil has an aromatic hydrocarbon content less than 20 wt %, preferably less than 10 wt %, and most preferably less than 1 wt %. The preferred neutralized sulfonated polymer elastomer is sulfonated EPDM terpolymer (defined below).

In the broadest aspect of the invention, the low toxicity drilling fluid of the present invention comprises four main components: (a) a petroleum oil, (b) an oil viscosifier, (c) aqueous phase, and (d) a surfactant for emulsifying water in oil. Optionally, the system may include other additives. Each of these components are described below.

(a) Petroleum Oil

The petroleum oils useful in the present invention are oils low in aromatics. These oils are available in the industry and are referred to by various names including "mineral oil", "low-toxicity oils", "low aromatic oils" and "low polynuclear aromatic oils", etc. These oils generally are complex mixtures of paraffins and naphthene hydrocarbons ranging from 12 to 36, preferably 18 to 36, carbon atoms.

As used herein the terms "low-toxicity oil" and "low aromatic oil" refer to oils containing less than 20 wt% aromatic hydrocarbons. Common examples of such oils may in fact contain less than 10 wt% and frequently only 1% or less of aromatic components.

Commercial low toxicity or low aromatic oils include mineral oils, whites oils, mineral seal oils, and isoparaffin oils, paraffin oils, and the like.

(b) Viscosifier

The purpose of the viscosifier is to improve the rheological properties of the mud, particularly the yield point and gel strength (as measured by initial gel strength) to suspend

particles therein.

As mentioned above, the viscosifier for the oil phase of the low toxicity mud is principally neutralized sulfonated elastomeric polymer. This polymer is useful over a range of application rates from 0.027 to 4.5 kg (0.05 to 10 pounds) per 159 litre (42 US Gallon) barrel ie kg/bbl (lb/bbl) of the oil base mud. The preferred rate of use of the polymer is 0.045 to 2.7 kg/bbl (0.1 to 6 lb/bbl) and it is most preferred to use the polymer at a rate of 0.18 to 1.4 kg/bbl (0.4 to 3 lb/bbl).

EPDM terpolymers, as defined according to the definition in ASTM D-1418-64, are unsaturated polymers having about 1 to about 10.0 wt% olefinic unsaturation, more preferably about 2 to about 8 wt%, and most preferably about 3 to 7 wt%. The term EPDM terpolymers is intended to mean interpolymers containing ethylene and propylene in the backbone and a diene in the side chain. Illustrative methods for producing these terpolymers are found in U.S. Pat. No. 3,280,082; British Pat. No. 1,030,289 and French Pat. No. 1,386,600, the disclosure of which are incorporated herein by reference. The preferred polymers contain about 40 to about 75 weight % ethylene and about 1 to about 10 weight percent of a diene monomer, the balance of the polymer being propylene. Preferably, the polymer contains about 45 to about 70 wt % ethylene, (e.g. 50 wt %) and about 2.6 to about 8.0 wt % diene monomer, (e.g. 5.0 wt %). The diene monomer is preferably a non-conjugated diene.

Illustrative of these non-conjugated diene monomers which may be used in the terpolymer (EPDM) are 1,4-hexadiene, dicyclopentadiene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 5-propenyl-2-norbornene, and methyltetrahydroindene.

A typical EPDM terpolymer, is Vistalon 2504 (marketed by Exxon Chemical Co.), a terpolymer having a Mooney viscosity (ML, 1 + 8, 212°F (100°C)) of about 40 and having an ethylene content of about 50 wt % and a 5-ethylidene-2-norbornene content of about 5.0 wt %. The number average molecular weight (Mn) as measured by GPC of Vistalon 2504 is about 47,000, the viscosity molecular weight (Mv) as measured by GPC is about 145,000 and the weight average

molecular weight (M_w) as measured by GPC is about 174,000.

Another EPDM terpolymer, Vistalon 2504-20, is derived from Vistalon 2504 (Exxon Chemical Co.) by a controlled extrusion process, wherein the resultant Mooney viscosity at 212°F (100°C) is about 20. The M_n as measured by GPC of Vistalon 2504-20 is about 26,000, the M_v as measured by GPC is about 90,000 and the M_w as measured by GPC is about 125,000.

Nordel 1320 (marketed by DuPont) is another terpolymer having a Mooney viscosity at 212°F (100°C) of about 25 and having about 53 wt % of ethylene, about 3.5 wt % of 1,4-hexadiene, and about 43.5 wt % of propylene.

The EPDM terpolymers used in the present invention have a M_n as measured by GPC of about 10,000 to about 200,00, more preferably of about 15,000 to about 100,00, and most preferably of 20,000 to about 60,000. The Mooney viscosity (ML, 1+8, 212°F (100°C)) of the EPDM terpolymer is about 5 to about 60, more preferably about 10 to about 50, and most preferably about 15 to about 40. The M_v as measured by GPC of the EPDM terpolymer is preferably below about 350,000 and more preferably below about 300,000. The M_w as measured by GPC of the EPDM terpolymer is preferably below about 500,000 and more preferably below about 350,000.

The elastomeric polymers are sulfonated by a process in a non-reactive solvent such as a chlorinated aliphatic solvent, chlorinated aromatic hydrocarbon, an aromatic hydrocarbon, or an aliphatic hydrocarbon, such as carbon tetrachloride, dichloroethane, chlorobenzene, benzene, toluene, xylene, cyclohexane, pentane, isopentane, hexane, isohexane or heptane. The preferred solvents are the lower boiling aliphatic hydrocarbons. A sulfonating agent is added to the solution of the elastomeric polymer and non-reactive solvent at a temperature of about -100°C to about 100°C for a period of time of about 1 to about 60 minutes, more preferably at room temperature for about 5 to about 45 minutes; and most preferably for about 15 to 30 minutes. Typical sulfonating agents are described in U.S. Pat. Nos. 3,642,726 and 3,836,511, the disclosures of which are incorporated herein by reference. These

sulfonating agents are selected from an acyl sulfate; a mixture of sulfuric acid and an acid anhydride; or a complex of a sulfur trioxide donor and a Lewis base containing oxygen, sulfur, or phosphorous. Typical sulfur trioxide donors are SO_3 , chlorosulfonic acid, fluorosulfonic acid, sulfuric acid, oleum, etc. Typical Lewis bases are: dioxane, tetrahydrofuran, tetrahydrothiophene or triethyl phosphate. The most preferred sulfonation agent for this invention is an acyl sulfate selected from the group consisting essentially of benzoyl, acetyl, propionyl or butyryl sulfate. The acyl sulfate can be formed in situ in the reaction medium or pregenerated before its addition to the reaction medium in a chlorinated aliphatic or aromatic hydrocarbon.

It should be pointed out that neither the sulfonating agent nor the manner of sulfonation is critical, provided that the sulfonating method does not degrade the polymer backbone. The reaction is quenched with an aliphatic alcohol such as cyclohexanol or with water. The unneutralized sulfonated elastomeric polymer has about 5 to about 30 meq. sulfonate groups per 100 grams of sulfonated polymer, more preferably about 5 to about 25; and most preferably about 5 to about 15. The range of sulfonate content does vary over an extremely broad latitude; however, it has been observed that in those systems of high sulfonation level there is great difficulty in dissolving the sulfonated polymers which can lead to very adverse effects in terms of the interaction of the sulfonated polymer with barite weighting agent and with other components of the drilling mud. Therefore, there is clearly an optimum level of sulfonation content which may vary from one sulfonated backbone to another, but for sulfonated EPDM, this optimum level is reached in the most preferred embodiment of the invention as described above. The meq. of sulfonate groups/100 grams of polymer is determined by both titration of the polymeric sulfonate acid and Dietert Sulfur analysis. In the titration of the unneutralized sulfonate, the polymer is dissolved in solvent consisting of 95 parts by volume of toluene and 5 parts by volume of methanol at a concentration of 50 grams per liter

of solvent. The unneutralized sulfonated polymer is titrated with ethanolic sodium hydroxide to an alizarin-thymolphthalein endpoint.

The unneutralized sulfonated polymer is gel-free and hydrolytically stable. Gel strength is measured by stirring a given weight of polymer in a solvent comprised of 95 wt % toluene 5 wt % methanol at a concentration of 5 wt % for 24 hours, allowing the mixture to settle, withdrawing a weighed sample of the supernatant solution, and evaporating to dryness.

Hydrolytically stable means that the unneutralized sulfonate will not be eliminated under neutral or slightly basic conditions to a neutral moiety which is incapable of being converted to highly ionic functionality.

Neutralization of the unneutralized sulfonate groups of the sulfonated elastomeric polymer is achieved by the addition of a solution of a basic salt to the unneutralized sulfonated elastomeric polymer dissolved in the mixture of aliphatic alcohol and non-reactive solvent. The basic salt is dissolved in a binary solvent system consisting of water and/or an aliphatic alcohol. The counterion of the basic salt is selected from antimony, iron, aluminum, lead and Groups IA, IIA, IB, or IIB of the Periodic Table of Elements and mixtures thereof, as well as ammonium and amine counterions. The preferred cations include zinc, magnesium, sodium, lead, barium, calcium, and ammonium cations, wherein zinc, magnesium and sodium are the most preferred cations. The anion of the basic salt is selected from a carboxylic acid having from about 1 to about 4 carbon atoms, a hydroxide, or alkoxide and mixtures thereof. The preferred neutralizing agent is a metal acetate, more preferably zinc acetate. Sufficient metal salt of the carboxylic acid is added to the solution of the acid form of the elastomeric polymer to effect neutralization. It is preferable to neutralize at least 95% of the acid groups, more preferably about 98%, and most preferably 100%.

Examples of metal oxides useful in preparing metal

sulfonates are MgO, CaO, BaO, ZnO, Ag₂O, PbO₂ and Pb₃O₄. Useful examples of metal hydroxides used in preparing metal sulfonated elastomeric polymers are NaOH, KOH, LiOH, Mg(OH)₂ and Ba(OH)₂.

(c) Aqueous Phase

The aqueous portion of the oil base drilling muds described herein provides the internal phase of an oil external emulsion and may be present in any proportion consistent with stability of the emulsion under the prevailing conditions of the drilling operation for which the mud is employed. Thus it is possible to use from a trace amount of aqueous phase to as much as 60% aqueous phase or more by volume of the liquid portion of the drilling fluid. Preferably, the aqueous phase of the muds of the present invention will be from 1 % to 40% by volume of the liquids; and most preferably will be between 5 to 30 vol %.

The aqueous phase of these muds may be fresh water; a sodium, calcium, or mixed brine; or other aqueous solution which provides a stable oil external emulsion drilling mud. The composition of the aqueous phase of the oil base mud is not critical to the function of the ~~present~~ invention. Typical oil base muds are made from a brine containing 25-35% by weight of calcium chloride. These brines are within the scope contemplated for the ~~present~~ invention. The remaining volume of the liquid portion of the drilling mud is occupied by the hydrocarbon base oil and liquid surfactant components.

(d) Surfactants

Surfactants used in the muds of the present invention include those additives suitable for forming and maintaining water-in-oil emulsions and also those which provide and maintain an oil wet surface on the solids suspended in the drilling fluid. Non-limiting examples of these two classes of chemicals are magnesium and calcium soaps of fatty acids, fatty imidazolines, fatty amines, fatty amides, polyamide derivatives, organic sulfonic acid derivatives, and ethylene and/or propylene oxide adducts. Also included in the class of oil wetting agents for suspended solids

are organic phosphates and a variety of amphoteric surfactants.

(e) Other Additives.

The oil base mud may include other additives such as weighting agents, fluid loss additives, etc. Barite (barium sulfate) and hematite (iron oxide) are typical weighting agents. Fluid loss additives include insoluble soaps, finely divided solids, asphalts, gilsonite, and organolignites.

In addition to the sulfonated EPDM terpolymer which is the principal viscosifier of the subject invention, there may be included in the muds of the invention optionally other viscosifiers. These other viscosifiers may be, for example, organophilic clays, asphalts, gilsonite, finely divided solids or other commonly used oil base mud viscosifiers. The use of these optional viscosifiers is complementary to the use of the sulfonated EPDM polymer of this invention and in no way interferes with the function of the EPDM polymer.

The low toxicity, oil-base drilling mud of the present invention is used in the drilling of subterranean wells, particularly in areas where ecology is an important consideration. Some of the principal characteristics of this mud which render it useful include the following: its formulation does not interact significantly with swelling, viscosity producing natural formation clays; it produces thin, hard, slick filter cakes when pressed against porous surfaces; and it exhibits considerable utility in the drilling of deep, high temperature earth formations. In addition, the mud of the present invention exhibits useful rheology which is surprising in view of the low aromaticity of the oil phase. The development of this rheology requires less heat and shear than for low aromatic content oil base muds containing viscosifiers of the prior art, e.g. organophilic clays.

These properties provide value to the subject formulations

for use in a variety of drilling operations. The following descriptions of particular operations are for illustrative purposes and describe three of many procedures for formulating and using the mud in the drilling of wells.

In a particular application of the present invention the oil mud base is prepared at a blending plant by emulsifying a brine into a low aromatic content base oil containing emulsifiers, the sulfonated EPDM terpolymer, and other ingredients as described above. The amount of the mud formula prepared may vary, but will normally fall into the range of 500 to 5,000 bbl, the selected volume depending on the volumes of the hole being drilled and of the surface tanks, pumping and treating equipment at the drilling site. The rapid increase in viscosity provided by the sulfonated EPDM terpolymer, in this otherwise difficult to viscosify system, enables the mud to support high density solids such as barite and/or hematite which are subsequently mixed with the mud at the blending plant and ensures suspension of these solids during shipment of the mud from the blending plant to the field drilling site.

Upon arrival at the drilling site, the mud is used to spud and drill a difficult well to completion or to displace a water base drilling fluid for the drilling of a difficult interval of a well. The difficulty in drilling a certain interval of a well or an entire well may be due to high temperature, earth formations sensitive to water, a highly deviated wellbore in which there is considerable friction and danger of pipe sticking when aqueous muds are used, or some other cause.

In another application of the invention, the sulfonated EPDM terpolymer is added to a conventional oil base mud, wherein the base oil is a low aromatic content oil, thereby converting the existing mud to a mud of this invention. The addition of this polymer may take place at a blending plant or during the use of the mud at a field drilling site and the conventional mud so treated may be freshly prepared or previously used in well drilling operations. The quantity of mud treated in this way will be

similar to that described for a new mud prepared in a blending plant as above. By converting the conventional mud to a formula of the type specified here there will be achieved superior viscosification of the mud than would be possible with organophilic clay or other conventional oil mud viscosifier.

The mud is continually mixed in the surface tanks or pits at the drilling site, pumped downhole through the drill pipe, out of the nozzles on the drill bit, and back up the annulus of the hole to the surface with formation cuttings. These cuttings will be separated from the mud mechanically, and the mud is then returned to the tanks.

In still another application, the mud of the present invention may be utilized as a packer fluid. As in the above operations the formulation is prepared in any of a number of ways: as a new fluid as described above for a drilling mud emulsified at a blending plant or by the addition of an existing oil base mud with the sulfonated EPDM terpolymer either in the field or at a blending plant. Normally higher quantities of the polymer are used for the packer fluid application than for drilling so that the solids suspended in the fluid may be supported with the fluid quiescent over a longer period of time. A well casing is more or less permanently filled with the packer fluid between two seals or packers so that the fluid supports the interior of the casing against formation or other stresses, during completion and/or production operations of a well.

Naturally it is understood that in order to maintain the desired quantities and properties of the drilling fluids described here over the course of their use in the field, additions of any of the components of the fluids may be made. Likewise, any of the required or optional components of the fluids may be added during the drilling operations to adjust the quantities and properties of the fluids whether or not those components were initially present in the fluid in the drilling operations.

Other operations relating to the use of the low toxicity mud of the present invention will become apparent to workers

skilled in the art.

EXAMPLES

Laboratory experiments were conducted to demonstrate the utility of the low toxicity mud. Four oil base muds were prepared representing four combinations containing a low or medium content aromatic oil and an organophilic clay or sulfonated EPDM terpolymer viscosifier. The mud recipes include one of the following Base Oils, one of the Viscosifiers, and Other Ingredients:

Base Oil A	182 ml of a very low aromatic mineral oil containing less than 1 wt% aromatic components.
Base Oil B	182 ml refined oil containing about 8 wt% aromatic components.
Viscosifier C	5.2g of organophilic bentonitic clay
Viscosifier D	1.0 g of sulfonated EPDM terpolymer
<u>Other Ingredients</u>	
Primary Emulsifier (Dresser "Oilfaze")	5.2 g
Secondary Emulsifier (Dresser "Oilfaze")	1.75 g
Ca (OH) ₂	1.75 g
CaCl ₂ , 25 wt/wt% aq	100 ml
Barite	290 g
Rev Dust	13 g

The base oil of the comparative samples 1, 3, 5, 7 (Table I) was placed in an osterizer brand blender and mixed with the viscosifier, for 5 min at low speed. The remaining ingredients were added and the mixture mixed for 10 min. For samples 2, 4, 6, and 8 the polymeric viscosifier was added to the blended base oil and other ingredients, and the final formulation

was blended for a 10 min period. The mud aliquots were aged for 16 hr in a roller oven at 150°F (165°C), cooled to room temperature, and remixed for 5 min. The rheology of each sample was measured at 115°F (45°C) on a Fann Model 35 Viscometer. The samples were then sealed in individual bombs and aged for 16 hr at 300°F (150°C). The cooling, stirring, and viscosity measurement were carried out as before. Results of the rheology measurements are given in the table below and show that the sulfonated EPDM terpolymer is a superior viscosifier to organophilic clay for inverse emulsion oil muds and that the performance of the polymer is relatively independent of the nature of the emulsion base oil.

TABLE I

	BASE OIL	VISCOSIFIER IDENTITY	AGING TEMP, °F(°C)	PLASTIC VISCOSITY, mPas	YIELD POINT lb/100 ft ² (Pa)	INITIAL GEL STRENGTH lb/100 ft ² (Pa)
1	A	C	150 (65)	21	10 (5)	7 (3)
2	A	D	150 (65)	36	48 (23)	44 (21)
3	B	C	150 (65)	20	30 (14)	17 (8)
4	B	D	150 (65)	37	34 (16)	22 (11)
5	A	C	300 (150)	22	8 (4)	7 (3)
6	A	D	300 (150)	32	22 (11)	17 (8)
7	B	C	300 (150)	20	14 (7)	10 (5)
8	B	D	300 (150)	30	22 (11)	12 (6)

The data presented in Table I support the following conclusions:

- (1) The clay viscosifier was not effective for oils with a very low aromatic content.
- (2) The clay viscosifier was partially effective in oil containing about 8% aromatics, but not as effective as EPDM.
- (3) EPDM viscosifier was effective in both the very low aromatic oil and the 8% aromatic oil.

The data demonstrate that the low toxicity mud of the present invention exhibits rheological properties which are particularly useful in drilling operations.

CLAIMS

1. An oil base drilling mud which comprises:
 - (a) a petroleum oil containing less than 20 wt % aromatic hydrocarbons;
 - (b) about 1 to 40 volume % of water emulsified as an internal phase in said oil;
 - (c) an effective amount of an oil soluble, water-insoluble viscosifier to substantially increase the yield point and gel strength of the water-in-oil emulsion, said viscosifier being a neutralized sulfonated EPDM terpolymer having a number average molecular weight of about 10,000 to about 200,000.
2. An oil base drilling mud according to claim 1 in which the neutralized sulfonated EPDM has from about 5 to about 300 meq. of sulfonate groups per 100 grams of neutralized sulfonated EPDM.
3. An oil base drilling mud according to either of the preceding claims, in which the neutralized sulfonated EPDM has from 15 to 25 meq. of sulfonate groups per 100 grams of the neutralized sulfonated EPDM.
4. An oil base drilling mud according to any of the preceding claims, in which the oil is selected from mineral oils, white oils and paraffin oils.
5. An oil base drilling mud according to any of the preceding claims, in which the EPDM is neutralized by a zinc, magnesium or sodium cation.
6. An oil base drilling mud according to any of the preceding claims, in which the viscosifier is present in an amount from 0.027 to 4.5 kg (0.05 to 10 pounds) per barrel of the mud.

7. An oil bas drilling mud acording to any of th preceding claims, in which the mud further contains barium sulfate.

8. An oil base drilling mud according to any of the preceding claims, in which the petroleum oil contains less than 10% by wt of aromatic hydrocarbons.

9. An oil base mud according to any of the preceding claims, in which the petroleum oil contains less than 5% by wt of aromatic hydrocarbon.

10. An oil base mud according to claim 1 substantially as hereinbefore described.